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TASK N° NR 051-775

STUDY OF SYNCHROTRON RADIATION FROM WET ELECTRODE SURFACES

Principal Investigators

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## Part 1

### A. Papers Submitted

1. Two Dimensional Compressibility of Electrochemically Adsorbed Lead on Silver (111).  
O.R. Melroy, M.F. Toney, G.L. Borges, M.G. Samant, J.B. Kortright, P.N. Ross,  
and L. Blum.  
*Surface Science*
2. The Two Dimensional One-Component Plasma in a Doubly-Periodic Periodic  
Background: Exact Results.  
F. Cornu, B. Jancovici, L. Blum.  
*J. Statistical Physics.*
3. Electric Microfield Distribution in Charged Fluids: Plasmas, Ionic, and Dipolar  
Mixtures.  
F. Vericat, Y. Rosenfeld, and L. Blum.  
*Journal of Chemical Physics*

### B. Papers Published in Refereed Journals

1. Surface EXAFS of Underpotentially Deposited Silver on Au (111) Electrodes.  
J.H. White, M.J. Albarelli, H.D. Abruna, L. Blum, O.R. Melroy, M.G. Samant, G.L.  
Borges, and J.G. Gordon, II.  
*Journal of Physical Chemistry* **92**, 4432 (1988).
2. In-Plane Structure of Underpotentially Deposited Copper on Gold (111) Determined  
by Surface EXAFS.  
O.R. Melroy, M.G. Samant, G.L. Borges, J.G. Gordon, II, L. Blum, J.H. White,  
M.J. Albarelli, M. McMillan, and H.D. Abruna.  
*Langmuir*, **4**, 728 (1988)
3. Geometrical Structure of Adlayers on Immersed Electrodes.  
J. G. Gordon II, O. R. Melroy, L. Blum.  
*Springer Series in Surface Science*, "Diffusion at Interfaces: Microscopic Concepts,"  
Vol. **12**, 172-181 (1988)
4. In-Situ Grazing Incidence X-Ray Diffraction Study of Electrochemically Deposited  
Pb Monolayers on Ag (111).  
M.G. Samant, M.F. Toney, G.L. Borges, L. Blum, and O.R. Melroy.  
*Surface Science Letters*, **193**, 129, (1988).
5. Grazing Incidence X-Ray Diffraction Study of Lead Monolayers on Silver (111) and  
Gold (111) Electrode/Electrolyte Interface.  
M.G. Samant, M.F. Toney, G.L. Borges, L. Blum, and O.R. Melroy.  
*Journal of Physical Chemistry*, **92**, 220, (1988).
6. Kinetics of Charge Transfer at Metal Electrolyte Interfaces: From Classical to Quantum  
Statistics.  
L. Blum, P.P. Schmidt, and M. Quijada.  
*International Journal of Quantum Chemistry*, **21**, 245, (1987).

7. A Strategy to Determine the Transition State of an Electron Transfer Reaction.

P.P. Schmidt and L. Blum.

*Chemical Physics Letters*, **140**, 370, (1987).

C. Books in Print

None

D. Books Published

None

E - F Patents

No patents filed or granted

G. Invited Conferences

L. Blum:

Session chairman, Gordon Research Conference on Water and Aqueous Solutions.

Aug. 1-5, 1988.

Session Chairman, Gordon Conference on Physical Electrochemistry, Aug. 8-12, 1988.

J.G. Gordon:

"Geometrical Structure of Adlayers on Immersed Electrodes," LASST-ACSIS workshop on Interface Phenomena, 'Diffusion at Interfaces: Microscopic Concepts,' August 18-22, 1987, Campobello Island, New Brunswick, Canada.

"In-Situ SEXAFS and X-ray Scattering from a Metal:Electrolyte Interface," symposium on Photochemical and Electrochemical Surface Science at the American Chemical Society meeting Sept. 3, 1987, New Orleans, La.

"In situ Determination of the Geometrical Structure of Adlayers on Electrodes by Surface EXAFS," symposium on 'Substrate Morphology - Single Crystal Surfaces' at the Electrochemical Society meeting, in Atlanta, May 15-19, 1988.

"Geometrical Structure of Adlayers on Immersed Electrodes," 4th International Fischer Symposium on 'Electrochemical Phase Formation and Dissolution,' June 16, 1988 in Karlsruhe, FRG.

O. R. Melroy:

"Application of Surface EXAFS to the In Situ Structural Determination of Electrochemical Interfaces", Electrochemical Society meeting, May 15-20, 1988, Atlanta Ga.

"Two Dimensional Compressibility of Electrochemically Adsorbed Lead on Silver (111)", symposium on 'Substrate Morphology - Single Crystal Surfaces' Electrochemical Society meeting, May 15-20, 1988, Atlanta Ga.

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"In-Situ Structural Determinations at Metal/Electrolyte Interfaces", Conference on Chemistry and Physics of Electrified Interfaces, August 29, 1988, Bologna, Italy.

"X-Ray Scattering from Electrochemical Interfaces", International Society of Electrochemistry, September 5, 1988, Glasgow, Scotland.

## Part II

### A. Funding History

October 1, 1981 - September 30, 1982	\$115,551.00
October 1, 1982 - September 30, 1983	\$118,366.00
October 1, 1983 - September 30, 1984	\$ 85,498.00
October 1, 1984 - September 30, 1985	\$130,008.00
October 1, 1985 - September 30, 1986	\$130,008.00
October 1, 1986 - September 30, 1987	\$134,869.00
October 1, 1987 - September 30, 1988	\$134,869.00

### B. Current Telephone Numbers

Lesser Blum	(809) 763-3390
Joseph Gordon	(408) 927-1266
Owen Melroy	(408) 927-2485

### C. Description

The purpose of this project is to experimentally probe and theoretically model the structure of the charged liquid solid:interface. X-rays from a synchrotron source are the experimental probe. Direct structural information about selected bonds in the electrode interface is obtained from grazing incidence fluorescence detected EXAFS. The absorption near edge structure provides information about the state of oxidation of the adatoms. Information on long range order of adlayers can be obtained from grazing incidence x-ray diffraction. Changes in both the structure and the oxidation state as a function of the potential will give information on the inner layer of the electrode interface which has been unavailable until now.

Theoretically, we have searched for more accurate equations for the simpler models such as the primitive and ion- dipole models. In particular, we intend to search for accurate, yet tractable theories for structured interfaces, in which the solvent has a tetrahedral coordination shell and the surface is not smooth. Furthermore, models for charge transfer processes will be studied

### D. Results

During 1987-88 we carried out successful in-situ EXAFS experiments, for silver underpotentially deposited on a gold(111) surface and bromide adsorbed on a silver(111) surface. Using in-situ grazing incidence x-ray scattering, we also measured the compressibility of a two dimensional lead layer on a silver(111) surface.

One of the purposes of studying Ag on Au(111) was to see whether the Ag-Au distance varied with potential. It did not. We also observed backscattering from oxygen, which we assign to water adsorbed at specific sites on the Ag surface. The silver-oxygen distance was also constant, independent of potential. The bromide data is being analyzed.

Theoretically, we studied an exactly solvable model, obtaining the first solution of a doubly periodic potential. Continuing with the kinetic theory work, we analyzed the problem of the electric microfield distribution in a model ionic solution. We obtained exact conditions for the distribution of the electric field in a cavity in a solution.

### E. Summary of Plans

We expect to be able to run several times during the next year at Stanford and, possibly, also get time at Brookhaven. Our intent is to study the structure of bromide on silver at two or more coverages to try to observe coverage driven structural changes. We also intend to further characterize the upd layers of Cu on Au at half coverage and in the absence of sulfate ions.

We plan to extend the x-ray diffraction studies to monolayers of thallium and bismuth on silver. We also intend to probe the effect of the substrate on these incommensurate adlayers, by studying Pb or some other metal on several different substrates.

We will pursue the work on the double layer, trying to develop simpler and more accurate theories for the primitive model, such as the bridge function MIINC, and also more realistic models that include structural features of the surface, as well as the solvent. We will start calculations on small clusters of metals that simulate the interface to determine the relative stability of models that are consistent with the experiments.

### F. Graduate Students

### G. Post-Doctorals

Mahesh G. Samant (IBM)  
Lung-shan Kau (IBM)

### H. Technical Reports Submitted

- #29. A Strategy to Determine the Transition State of an Electron Transfer Reaction.  
P.P. Schmidt and L. Blum. *Chemical Physics Letters*, **140**, 370, (1987).
- #30. The Two Dimensional One-Component Plasma in a Doubly-Periodic Periodic Background: Exact Results.  
F. Cornu, B. Jancovici, and L. Blum. *J. Statistical Physics*.
- #31. Surface EXAFS of Underpotentially Deposited Silver on Au (111) Electrodes.  
J.H. White, M.J. Albarelli, H.D. Abruna, L. Blum, O.R. Melroy, M.G. Samant, G.L. Borges, and J.G. Gordon, II.  
*Journal of Physical Chemistry*
- #32. Two Dimensional compressibility of Electrochemically Adsorbed Lead on Silver (111).  
O.R. Melroy, M.F. Toney, G.L. Borges, M.G. Samant, J.B. Kortright, P.N. Ross, and L. Blum. *Surface Science*
- #33. In-Plane Structure of Underpotentially Deposited Copper on Gold (111) Determined by Surface EXAFS.  
O.R. Melroy, M.G. Samant, G.L. Borges, J.G. Gordon, II, L. Blum, J.H. White, M.J. Albarelli, M. McMillan, and H.D. Abruna. *Langmuir*.